

Application of a Rapid Chemical Oxygen Demand Test for Determining Organic Pollutions^{*+}

JANET B. PEPINSKY, NANDOR PORGES AND SAM R. HOOVER

U. S. Department of Agriculture
Eastern Regional Research Laboratory**
Philadelphia, Pennsylvania.

A rapid chemical oxygen demand method for determining the strength of organic wastes has been proposed by Porges, Pepinsky, Hendler and Hoover for use in the dairy industry⁸. Other chemical oxygen consumed tests are available, but they require more time than is desirable for empirical procedures. Dichromate methods similar to those first used by Adeney and Dawson¹ and von Fellenberg³ have been developed by Rhame⁹ and Ingols and Murray⁴. A further modification has been devised by Moore, Kroner, and Ruchhofs⁶. The Standard Method approved by the American Public Health Association and the American Water Works Association is based on oxygen consumed from permanganate². Also available is the Johnson, Halvorson and Tsuchiya modification⁵ of the iodic acid method. Previous reports give the use of a modification of Rhame's procedure which was developed by Eldridge⁸. This report constitutes a study of the accuracy of the method and its sensitivity to variations in experimental procedure. The extent of oxidation of some organic materials has been determined.

METHOD

Reagents

1. Dichromate oxidizing agent is prepared by dissolving 2.5 grams of potassium dichromate in a mixture of 500 ml. each of concentrated H_2SO_4 and 85 per cent ortho H_3PO_4 .
2. Potassium iodide solution is made by dissolving 55.3 grams of KI in 200 ml. of distilled water.

* Report of a study made under the Research and Marketing Act of 1946.
+ Presented at the American Chemical Society Meeting-in-Miniature, Philadelphia, Pa., January 1951.

** One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

3. Sodium thiosulfate solution—0.05 normal (0.100 N, 24.820 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter, diluted 1:2 daily.)
4. Starch solution—1 per cent (good grade of soluble starch which gives a true blue color with iodine).

PROCEDURE

1. Place exactly 50 ml. of the dichromate oxidizing solution in a 500-ml. Phillips beaker. Experience has shown that it is preferable to measure this solution from a 50-ml. automatic buret.
2. Transfer 5 ml. of the waste sample to the beaker (for a C. O. D. between 10-3000 ppm).
3. Place beaker on hot plate which has been preheated to the required temperature and suspend thermometer in solution.
4. Heat with frequent swirling so that the temperature of 165°C . is reached in six minutes.
5. Remove to water bath and cool to approximately room temperature.
6. Add 200 ml. of distilled water with care and again cool in bath to room temperature.
7. Add 10 ml. of the iodide solution and titrate with 0.05 N. sodium thiosulfate, adding the starch near the end point. The color changes from blue to green.
8. A blank determination, in which 5 ml. of distilled water is used, is run through the same procedure.
9. The total chemical oxygen demand expressed as parts per million or milligrams per liter is equal to 80 times the difference in ml. of 0.05 N sodium thiosulfate used by the water blank and sample.

$$\text{C.O.D.} = \frac{\text{ml. Na}_2\text{S}_2\text{O}_3 \text{ in blank} - \text{ml. Na}_2\text{S}_2\text{O}_3 \text{ in sample} \times 0.05 \times 8 \times 1000}{5 \text{ ml. sample}}$$

RESULTS

Solutions were prepared containing 1000 ppm of water-soluble organic compounds. For the water-insoluble organic materials, a 5-mg. sample was weighed in a micro weighing vessel and placed directly in the chromic acid solution, together with 5 ml. of distilled water.

As noted in Table 1, acetic acid was only slightly oxidized by this method; the other three monocarboxylic acids were more highly oxidized. The oxidation values of 85 per cent for both butyric and oleic acids agree

well with the value for butter, which is discussed later in the paper. The value of 63 per cent for stearic acid is lower than was expected. The nine per cent oxidation of acetic acid obtained in this study is consistent with the five per cent oxidation reported by Moore, Kroner, and Ruchhoft⁶. Others have also reported low values for this acid. Moore, Ludzak and Ruchhoft report 95 per cent oxidation by chromic acid refluxed for two hours in the presence of silver sulfate catalyst⁷. After this paper was ready for publication, determinations using acetic acid and silver sulfate catalyst were made. Complete oxidation was obtained when 0.2 grams silver sulfate was added to the digestion solution. Owing to the precipitation of silver iodide, the end point was difficult to obtain unless the starch was used as an outside indicator.

TABLE 1
OXIDATION OF 1000 PPM OF MATERIAL

Compound	Theoretical ppm O ₂	Experimental ppm O ₂	% of Theoretical
Acetic acid	1070	100	9
Butyric acid	1820	1550	85
Stearic acid	2930	1850	63
Oleic acid	2890	2450	85
Ethyl alcohol*	700	654	94
Lactic acid*	670	660	98
Glycine	640	250	39
Leucine	1830	1470	80
Tyrosine	1680	1610	96
Glutamic acid	980	800	82
Glucose	1070	1030	96
Lactose	1060	1040	98
Cellulose	1115	1115	100

* Theoretical calculated to acetic acid.

When calculations were based on acetic acid formation instead of complete oxidation, oxidation values of 94 and 98 per cent were obtained for ethyl alcohol and lactic acid. The data indicate that practically none of these volatile materials were lost in this method.

The carbohydrates were easily oxidized to completion by this procedure.

The amino acids were not completely oxidized, especially glycine, which was only 39 per cent oxidized. Values for leucine, tyrosine and

glutamic acid, 80, 96, and 82 per cent respectively, showed more complete oxidation.

The question was raised whether partial oxidation of amino acids to stable products took place or whether incomplete oxidation occurred under these experimental conditions. Table 2 shows the results when different temperatures and heating times are used on glycine. The theoretical value is that for oxidation to carbon dioxide and ammonia. There is no apparent explanation for the oxidation value of 120 per cent obtained under the most drastic heating conditions; a check experiment did not indicate that ammonia was oxidized. The low value obtained by heating for 6 minutes to 165° C., which is the normal procedure, can be attributed to incomplete oxidation of this refractory amino acid.

TABLE 2
OXIDATION OF 1000 PPM OF GLYCINE

Heating Conditions	Experimental, ppm	% of Theoretical
6 min. to 165° C.	240	38
9 min. to 185° C.	550	86
3 min. to 185° C. + 3 min.	670	105
5 min. to 185° C. + 4 min.	765	120

Table 3 shows the noticeable titration differences obtained when water blanks were subjected to the same conditions as the glycine samples. Samples and blanks should always be run under similar conditions.

TABLE 3
EFFECT OF HEATING ON BLANK

Heating Conditions	M1. 0.05 N. Sodium thiosulfate
Cold blank	48.90
6 min. to 165° C.	48.25
9 min. to 190° C.	47.07

Since the object of these studies was the biological oxidation of dairy wastes⁸, determinations were made on butter, casein and lactose under different conditions of heating time and temperature. By the method (six minutes-165°C.) 88, 85 and 98 per cent oxidation was obtained for butter, casein and lactose respectively (Table 4); heating to 190°C. for nine minutes altered the values only to 95, 90 and 94 per cent.

TABLE 4
EFFECTS OF TIME AND TEMPERATURE
ON OXIDATION OF 1000 PPM OF DAIRY PRODUCTS

Sample	Moisture %	Calculated ppm	Experimental Conditions		
			3 min-150° C. ppm	6 min-165° C. ppm	9 min-190° C. ppm
Butter	15.5	2370	1850	2100	2240
Air-dried casein..	8	1360	1020	1150	1230
Lactose-hydrate ..	5	1060	1030	1040	1000

The applicability of this procedure to other industrial wastes was also considered. In view of the possibility that the method might be used for oil refinery wastes, it was tried on a representative sample of waste from a refinery. Table 5 compares the result with the results obtained by the iodate and B. O. D. methods. The result was 84 per cent of the former and 258 per cent of the latter. Although the waste was not completely oxidized by this method, it appears that the proposed procedure can be used as a rapid means of estimating the pollution from this type of waste.

TABLE 5
OXIDATION OF CAUSTIC REFINERY WASTES

Method	Oxidation, ppm
Proposed	46,900
Iodate*	56,200
5-day B.O.D.*	18,200

* Courtesy of Mr. Roy Weston, Atlantic Refining Company.

Wastes from soap manufacture were studied to see if the method could be successfully used with these strong materials. Little information was available about the samples except that they might contain large amounts of inorganic salts, mainly sodium chloride. Direct determinations for B. O. D., C. O. D., total solids, volatile solids and sodium chloride were made and a C. O. D. determination was made on the ash left from the volatile solids (Table 6). The amount of sodium chloride present was so great that a determination for its oxygen demand was made. Theoretical oxidation was obtained (1 ppm C. O. D. = 7.3 ppm NaCl), as was expected from the data of Moore, Kroner, and Ruchhoft⁶, who obtained complete oxidation by using milder conditions than are employed in this procedure.

TABLE 6
OXIDATION OF SOAP PLANT WASTES

	From Soap Stock Re- ceiving Tank	From 1st Wash Kettle	From 2nd Wash Resin Kettle	From Strong Caustic Wash Tank
Total C.O.D., ppm.	19,400	50,820	73,960	186,960
5-day B.O.D., ppm.....	5,790	24,380	31,380	113,000
Total solids, ppm.....	159,450	215,300	217,350	184,650
Volatile solids, ppm.....	9,000	17,000	33,100	67,700
NaCl (by direct det'n), ppm.....	115,800	53,200	54,800	14,950
C.O.D. of ash, ppm.....	11,700	5,800	6,000	1,830
NaCl (indirectly de- termined*), ppm.	85,410	42,340	43,800	13,360
Corrected C.O.D.**, ppm.....	7,700	45,020	67,960	185,130
Ratio of corr. C.O.D. to vol. sol.	0.86	2.6	2.1	2.7
Ratio of B.O.D. to vol. sol.....	0.64	1.37	0.95	1.67
Ratio of B.O.D. to corr. C.O.D.....	0.74	0.54	0.46	0.61

* C.O.D. of ash x 7.3.

** Total C.O.D. minus C.O.D. of ash.

These results demonstrate that the method is applicable to soap plant wastes if a correction is made for oxidation of chloride. The salt content ranged from approximately 1.5 to 10 per cent, as determined volumetrically¹⁰; slightly lower amounts were indicated by applying the C. O. D. determination to the ash from the volatile solids determination. The validity of the results is best demonstrated by comparing the ratios of the 5-day B. O. D. to the corrected C. O. D. The corrected C. O. D. approximates the 20-day B. O. D. or complete oxidation; the 5-day B. O. D. would therefore be expected to be about 50 to 70 per cent of the corrected C. O. D. The determined ratio of 0.46 to 0.75 on these samples is a confirmation of the experimental procedure.

At the suggestion of Dr. C. L. Ogg, of this Laboratory, the reproducibility of this method was tested by running a series of blanks and replicate determinations. The results of five blank determinations and 10 replicates, in which a solution of 0.1 per cent dried skim milk solids was used, are shown in Table 7.

The mean value of the 10 replicates was 1073 ppm with a standard deviation (s) of ± 13 ppm. By the usual statistical theory, this shows that a deviation no greater than ± 13 ppm (1S) from the mean can be expected two times out of three, or ± 26 ppm (2S) 19 times in 20 replicates. These deviations are respectively ± 1.2 and ± 2.4 per cent of the mean value. The determinations were made by the senior author after more than two years' experience with the procedure.

TABLE 7
REPRODUCIBILITY OF C.O.D. METHOD ON 1000 PPM
OF AIR-DRIED SKIM MILK

Blank	0.05 N Na ₂ S ₂ O ₄ ml.	C.O.D. ppm
1	47.42	
2	47.42	
3	47.39	
4	47.40	
5	47.40	
mean 47.41		
Sample		
1	34.20	1057
2	34.00	1073
3	34.03	1060
4	34.20	1057
5	34.00	1073
6	33.80	1089
7	34.05	1067
8	34.11	1064
9	33.80	1089
10	33.83	1086
		mean 1073 ppm
		Standard deviation 13 ppm*

* The square of the standard deviation is equal to the sum of the squares of the difference between the mean value and the determined value divided by the number of determinations minus one.

DISCUSSION

More precise results may possibly be obtained by one of the procedures which involves lengthy refluxing of the oxidizing solution than by this procedure. The extent of oxidation is comparable, for in this rapid procedure water is driven off and a higher temperature is reached than in refluxing methods. The primary advantages of the rapid procedure are reproducibility, speed and simplicity of equipment and operation. The entire procedure is carried out in a 500-ml. Phillips pyrex beaker without transfer of the solution. This beaker was chosen because of its flat bottom, convenient size and shape, and relatively thin walls which allow rapid heating and cooling. A 500-ml. Erlenmeyer flask might be used, but such flasks usually have thicker walls and are rounded on the bottom.

SUMMARY

The extent of oxidation of a series of typical carbohydrates, proteins and fatty compounds by the rapid chemical oxidation procedure previously described has been determined. The effects of rate and extent of heating and of contaminating chlorides were measured.

The method can be successfully applied to dairy wastes, oil refinery waste and soap plant wastes to give approximate values of the total pollution.

The general use of this rapid procedure is suggested for experimental studies and measurements of pollution in plant and field studies of organic industrial wastes.

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